

Diatomic vibrating rotator

A molecule rotates while executing vibrational motion and therefore rotational energy changes may also accompany vibrational energy change. Consequently each vibrational band is found to contain rotational fine structure. As the energies of vibrational and rotational motions differ considerably, a diatomic molecule can execute both rotations and vibrations independently. Excluding electronic energy

$$E_{\text{total}} = E_{\text{rot}} + E_{\text{vib}} + \bar{\epsilon}_e = \bar{\epsilon}$$

$$E_{j,v} = E_J + E_v = \bar{\epsilon}$$

$$E_{j,v} = B J(J+1) - D J^2(J+1)^2 + (v + \frac{1}{2}) \bar{\nu}_e$$

$$\text{energy of } v \rightarrow (v + \frac{1}{2})^2 \bar{\nu}_e \text{ cm}^{-1} \quad \text{--- (1)}$$

where $J = 0, 1, 2, \dots$ and $V = 0, 1, 2, \dots$

The selection rule for combined motions, are the same as those for separate motion that is

$$\Delta V = \pm 1, \pm 2, \dots \text{ and } \Delta J = \pm 1$$

Only under very special circumstances $\Delta J = 0$ is allowed. $\Delta V = 0$ correspond to pure rotational transition. Vibrational changes must be accompanied by a simultaneous rotational change.

Assigning B and D the same for both $v=0$ and $v=1$ states and denoting upper state by single prime and lower state by double prime.

$$\bar{\nu} = \frac{1}{2} [B J'(J'+1) - D J'^2(J'+1)^2] - \frac{1}{2} [B J''(J''+1) - D J''^2(J''+1)^2] + \frac{1}{2} [(1+\frac{1}{2})\bar{\nu}_e - (1+\frac{1}{2})^2 x_e \bar{\nu}_e] - \frac{1}{2} [(0+\frac{1}{2})\bar{\nu}_e - (0+\frac{1}{2})^2 x_e \bar{\nu}_e]$$

$$\bar{\nu} = \left\{ B \left[J'(J'+1) - J''(J''+1) \right] - D \left[J'^2(J'+1)^2 - J''^2(J''+1)^2 \right] \right\} + \left(\frac{3}{2} \bar{\nu}_e - \frac{1}{4} x_e \bar{\nu}_e \right) - \left(\frac{1}{2} \bar{\nu}_e - \frac{1}{4} x_e \bar{\nu}_e \right) \text{ cm}^{-1}$$

$$= \bar{\nu}_e (1 - 2x_e) + B (J' - J'') (J' + J'' + 1) - D [J'^2(J'+1)^2 - J''^2(J''+1)^2] \text{ cm}^{-1}$$

Use the selection rule $\Delta J = +1$ i.e. $J' - J'' = 1$

$$\bar{\nu}_R = \bar{\nu}_0 + 2B (J''+1) - 4D (J''+1)^3 \text{ cm}^{-1} \quad \text{gives}$$

$$\Delta J = -1 \text{ i.e. } J' - J'' = -1 \quad \text{gives} \quad \text{--- (2) } \quad J'' = 0, 1, 2$$

$$\bar{\nu}_P = \bar{\nu}_0 - 2B (J'+1) + 4D (J'+1)^3 \text{ cm}^{-1} \quad \text{--- (3) } \quad J' = 0, 1, 2$$

Where $\bar{\nu}_0 = \bar{\nu}_e (1 - \frac{1}{2} 2x_e)$ is the frequency of the $v=0 \rightarrow v=1$ transition.

Lines corresponding to $\Delta J = -1$ are called the P branch and those corresponding to $\Delta J = +1$ are referred as R branch. This arbitrary notation is part of the sequence O, P, Q, R and S corresponding to $\Delta J = -2, -1, 0, +1, +2$ respectively.

Lines arising from $\Delta J = -2, -1, 0, +1, +2$ called O P Q R S

The frequency $\bar{\nu}_0$ is called the band centre or band origin

Equations (2) and (3) may be combined into a single equation

$$\bar{\nu}_{P,R} = \bar{\nu}_0 + 2Bm - 4Dm^3 \text{ cm}^{-1}$$

Usually, D is extremely small

$$m = \pm 1, \pm 2, \pm 3$$

Where $\bar{\nu}_{P,R} = \bar{\nu}_0 + 2Bm$
 m replaces $J''+1$ in eqn (2) and $J'+1$ in eq (3). Since $m \neq 0$ line at $\bar{\nu}_0$ will not appear. It requires J' and J'' to be -1 it is not possible. Lines to the low frequency side of $\bar{\nu}_0$ corresponding to negative m i.e. ($\Delta J = -1$) and referred to as the P branch.

While those to the high-frequency side are ($m +ve$, $\Delta J = +1$) called the R branch

Lines arising from $\Delta J =$

-2	-1	0	+1	+2	
called:	0	P	Q	R	S

Eqn (3) represents combined vibration-rotation spectrum. It consists of equally spaced lines (spacing = $2B$) on each side of the band origin $\bar{\nu}_0$.

The P and R notation with the lower J (J'') value as a suffix is illustrated in fig.

Analysis of the vibration-rotation spectrum of a diatomic molecule allows one to determine the band centre $\bar{\nu}_0$ and B from the spacing between the lines. From B one can calculate the bond length and from $\bar{\nu}_0$ the bond force constant.

Often the lines with maximum intensity may not be the first one in the P and R branches. It is due to the degeneracy of rotational states. Taking ~~degeneracy~~ ~~account~~ Since $m = J+1$ the maximum population is for the m value

$$m = \sqrt{\frac{KT}{2hcB}} + \frac{1}{2}$$

$$\bar{\nu}_{\text{max. inten}} = \bar{\nu}_0 + 2B \left(\sqrt{\frac{KT}{2hcB}} + \frac{1}{2} \right)$$

The separation between the maxima in the P and R branches is

$$\begin{aligned} \Delta\bar{\nu} &= 4B \left(\sqrt{\frac{KT}{2hcB}} + \frac{1}{2} \right) \\ &= \sqrt{\frac{8KT}{hc}} + 2B \end{aligned}$$

This procedure offers a method to estimate the rotational constant B

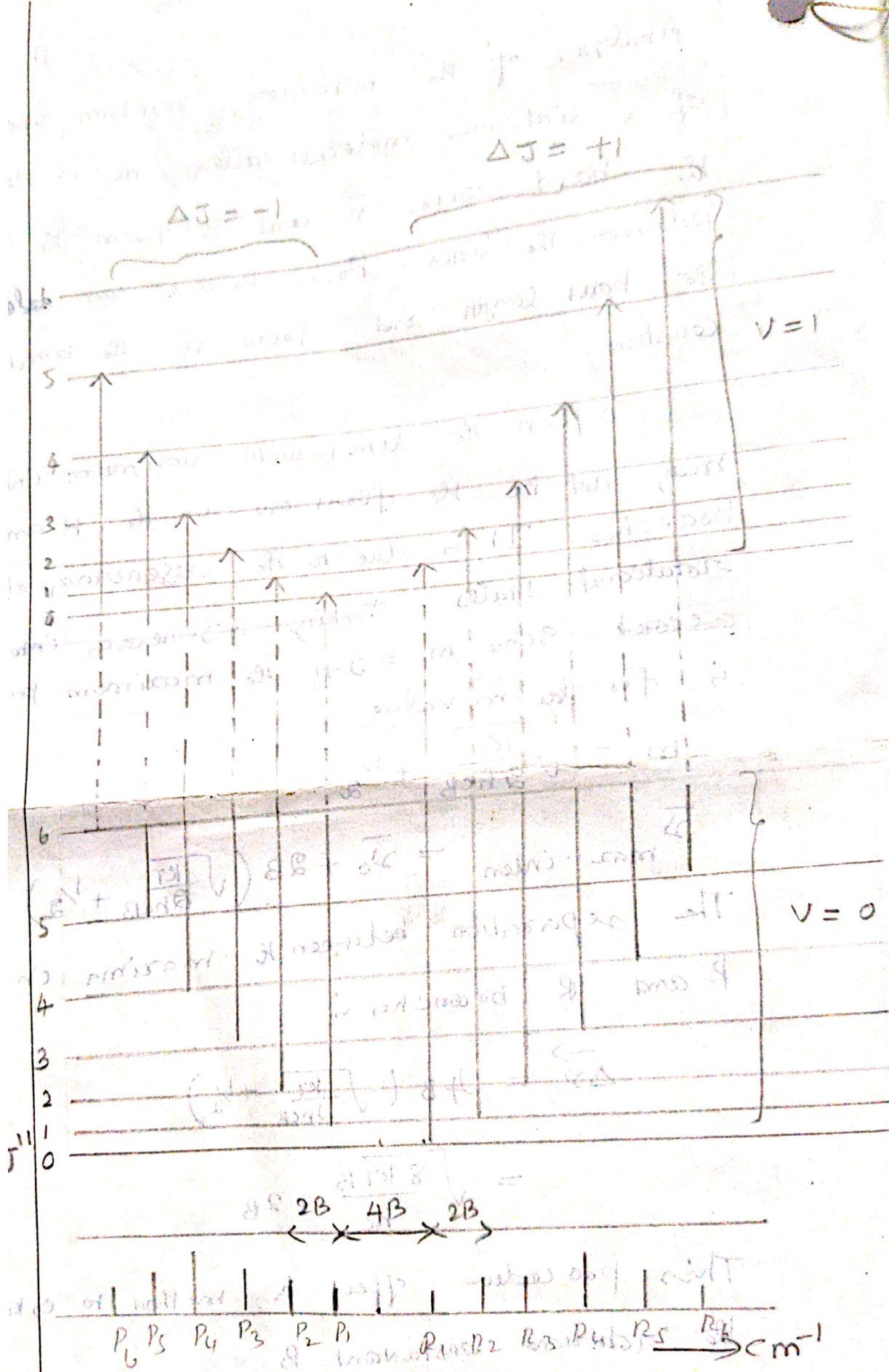


Fig: Some transition between the rotational - vibrational energy levels of a diatomic molecule together with the spectrum arising from

Applications of Infrared Spectroscopy

1) Identification of an organic compound

The identity of an organic compound can be established from its finger print region ($400 - 900 \text{ cm}^{-1}$). The identity of an organic compound is confirmed if its finger print region ~~is~~ exactly matches with the spectrum of that compound.

2. Structure determination

This technique helps to establish the structure of an unknown compound. All major functional groups absorb at their characteristic wave numbers. The shift due to environmental effects may also be looked into. From the data available due to absorption frequencies, the probable structure can be predicted. If some chemical data is available, it can lead to the confirmation of structure. It is known that the infra-red

more lowering in ...
1) Distinction between two types of hydrogen bonding

This technique is quite valuable to distinguish between the two types of hydrogen bonding.

It may be noted that the strength of the hydrogen bond is maximum when the proton donor group and the axis of lone pair orbital are collinear and varies inversely to the distance between X and Y (where X is hydrogen containing group and Y is Oxygen, nitrogen or halogen atom).

6. Presence of water in a sample

If a sample contains lattice water, its IR spectrum will contain three characteristic bands: one in the 3600 to 3200 cm^{-1} , second in the 1650 cm^{-1} region and the third in the $600 - 300\text{ cm}^{-1}$ region. On the other hand if the water is co-ordinated to a metal ion, an additional band in the $880 - 650\text{ cm}^{-1}$ region is observed.

Determination of purity or detection of impurity in a compound

Whenever a compound is having an impurity, it reduces the sharpness of individual bands, causes the appearance of extra bands and a general blurring of spectrum. It is useful for production control of many chemicals.

11. Quantitative analysis

It helps to make a quantitative estimation of an organic mixture. The estimation of the components of a mixture can be done by:

- (i) measuring the intensities of absorption bands characteristic of each component
- (ii) knowing the optical density of the absorption band for a pure component.